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(54) **INDUCTIVELY COUPLED PLASMA MASS SPECTROMETER**

(75) Inventors: **Kenichi Sakata**, Tokyo (JP); **Noriyuki Yamada**, Tokyo (JP)

(73) Assignee: **Agilent Technologies, Inc.**, Santa Clara, CA (US)

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H01J 49/12 (2006.01)
(52) **U.S. Cl.** **250/288**; 250/281; 250/282; 250/290
(58) **Field of Classification Search** 250/281, 250/282, 288, 289
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,948,962 A * 8/1990 Mitsui et al. 250/288

5,185,523 A	*	2/1993	Kitagawa et al.	250/281
5,308,977 A	*	5/1994	Oishi et al.	250/288
5,495,107 A	*	2/1996	Hu et al.	250/281
5,519,215 A	*	5/1996	Anderson et al.	250/288
6,265,717 B1	*	7/2001	Sakata et al.	250/289
6,936,787 B2	*	8/2005	Tao et al.	219/121.51
2004/0195218 A1	*	10/2004	Tao et al.	219/121.51
2006/0024199 A1	*	2/2006	Tao et al.	422/54
2006/0087651 A1	*	4/2006	Montaser et al.	356/338
2008/0099671 A1	*	5/2008	Sakata et al.	250/288

FOREIGN PATENT DOCUMENTS

|		
JP	10-188877	7/1998
JP	10-208691	8/1998
JP	11-006788	1/1999

* cited by examiner

Primary Examiner—David A Vanore
Assistant Examiner—Michael Maskell
(74) *Attorney, Agent, or Firm*—Marc Bobys

(57) **ABSTRACT**

An inductively coupled plasma mass spectrometer comprises a control device **70** for collectively controlling each of the following factors: the amount of liquid drops in the aerosol that is to be supplied to a plasma torch **20**, the flow rate of carrier gases **76**A and **76**B in this aerosol, the RF output of a high-frequency power source **80**, and the distance Z between plasma torch **20** and sampling interface **15** and **16**.
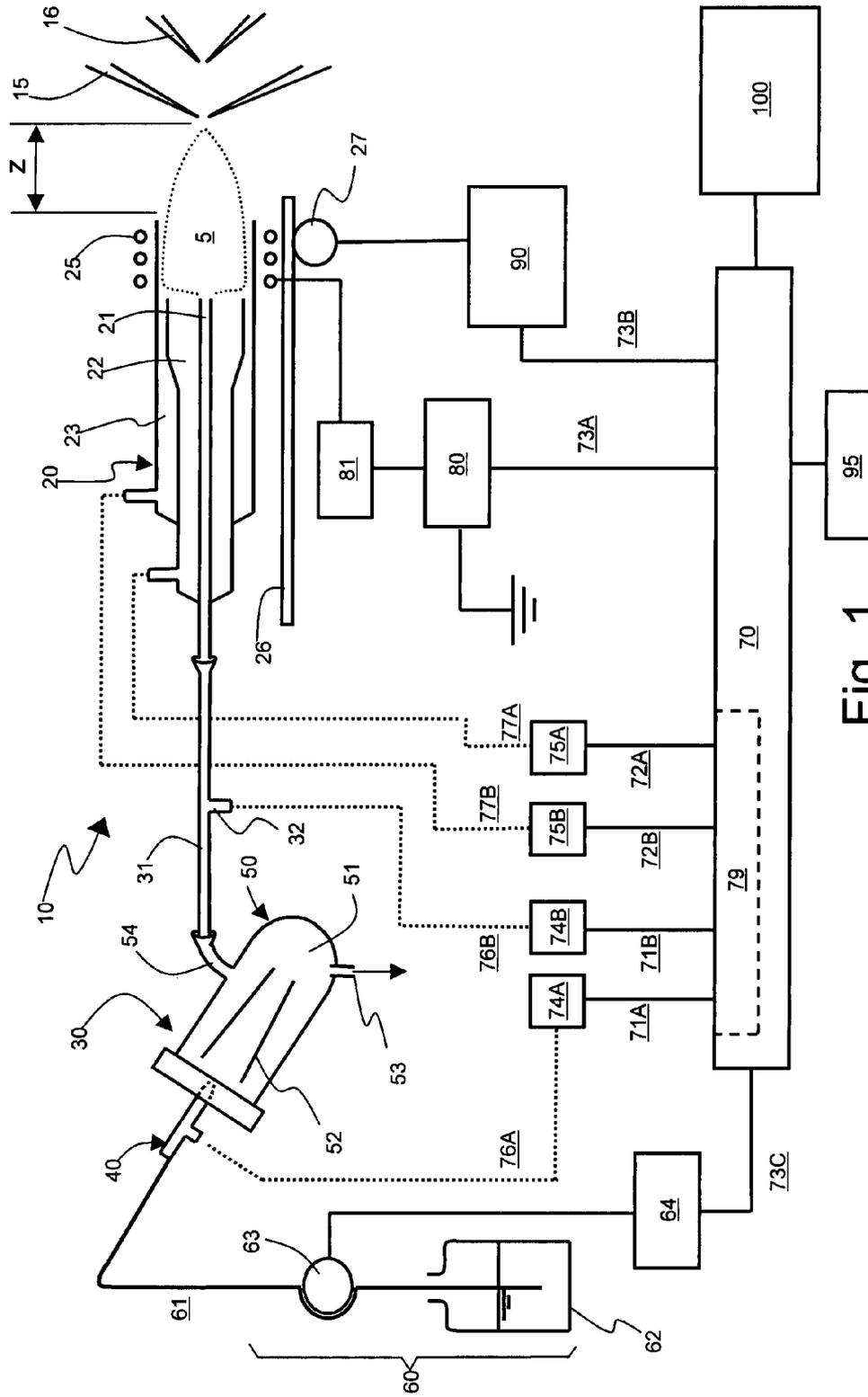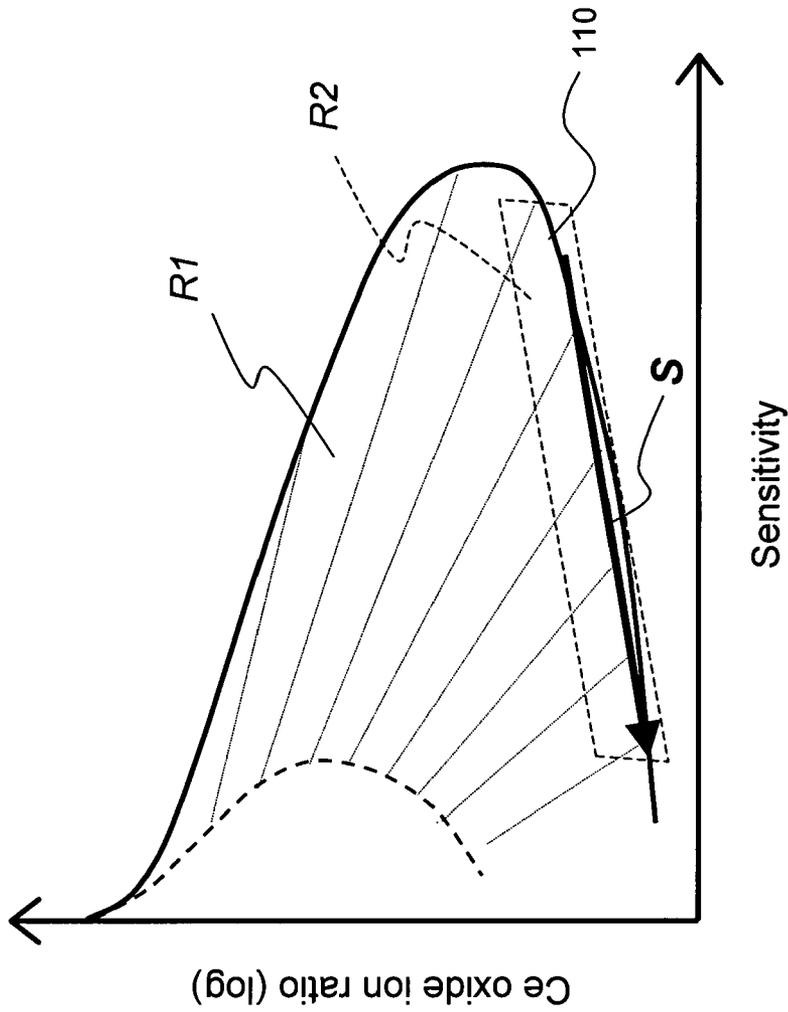
7 Claims, 6 Drawing Sheets
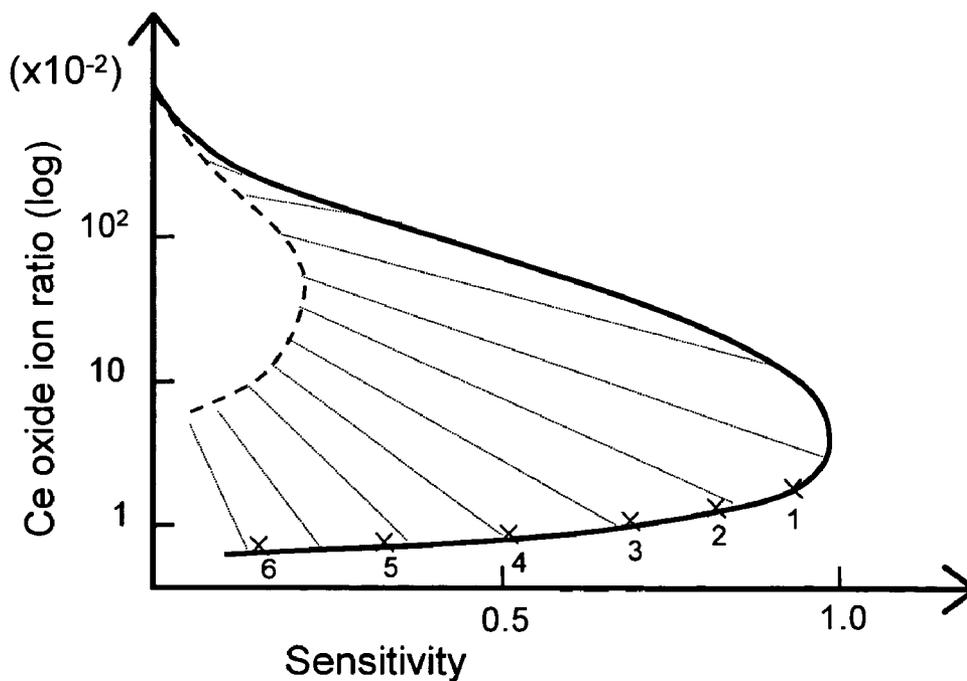
Fig. 1

Fig. 2

Mode	RF output (W)	Z(mm)	Carrier gas total Flow rate (L/mm)	Ce ion sensitivity (standardized)	Ce/CeO sensitivity ratio (x 10-2)
1	1550	5.5	1.06	0.84	1.16
2	1500	7.0	1.09	0.67	1.13
3	1500	8.0	1.09	0.54	1.01
4	1500	8.0	1.05	0.44	0.93
5	1400	9.0	0.95	0.21	0.81

Fig. 3a

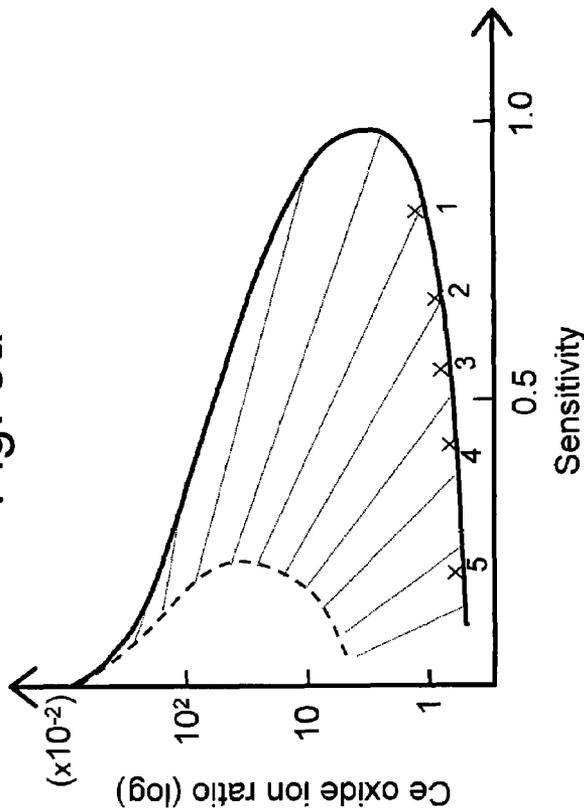Fig. 3b

Mode	RF output (W)	Z(mm)	Carrier gas total Flow rate (L/mm)	Ce ion sensitivity (standardized)	Ce/Ce0 sensitivity ratio (x 10-13)
1	1600	5.0	1.09	0.97	1.55
2	1600	6.0	1.11	0.86	1.33
3	1600	7.0	1.11	0.72	1.12
4	1600	8.0	1.09	0.52	0.98
5	1600	9.0	0.05	0.33	0.82
6	1600	10.0	0.95	0.15	0.74

Fig. 4a

Fig. 4b

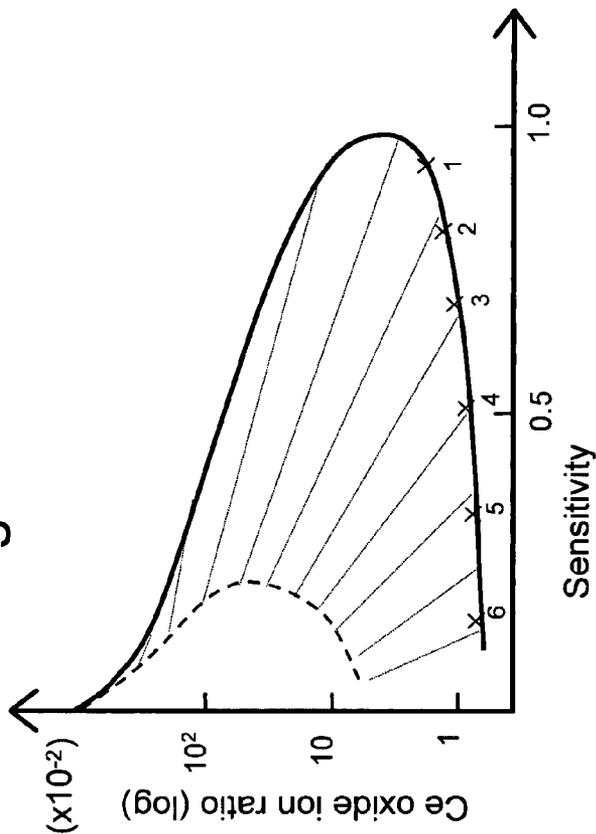| Mode	A	B	C	D	E
Aerosol-generating gas flow rate (mL/min)	1.05	0.55	0.40	0.30	0.20
Additional diluting gas flow rate(mL/min)	0.00	0.50	0.65	0.75	0.85
Carrier gas total flow rate (mL/min)	1.05	1.05	1.05	1.05	1.05
Volume of sample introduced (mL/min)	0.33	0.33	0.17	0.17	0.17
Sensitivity (standardized)	1	1/2	1/4	1/10	1/20

Fig. 5a

Mode	A	B	C	D	E
Aerosol-generating gas flow rate (mL/min)	1.05	0.95	0.50	0.30	0.30
Additional diluting gas flow rate(mL/min)	0.00	0.00	0.45	0.65	0.65
Carrier gas total flow rate (mL/min)	1.05	1.95	1.95	1.95	1.95
Volume of sample introduced (mL/min)	0.33	0.33	0.33	0.17	0.07
Sensitivity (standardized)	1	1/2	1/4	1/10	1/20

Fig. 5b

Mode	A	B	C	D	E
Aerosol-generating gas flow rate (mL/min)	0.95	0.50	0.30	0.20	0.20
Additional diluting gas flow rate(mL/min)	0.00	0.45	0.65	0.75	0.75
Carrier gas total flow rate (mL/min)	0.95	0.95	0.95	0.95	0.95
Volume of sample introduced (mL/min)	0.33	0.33	0.17	0.17	0.07
Sensitivity (standardized)	1	1/2	1/4	1/10	1/20

Fig. 5c

Mass-analyzing means
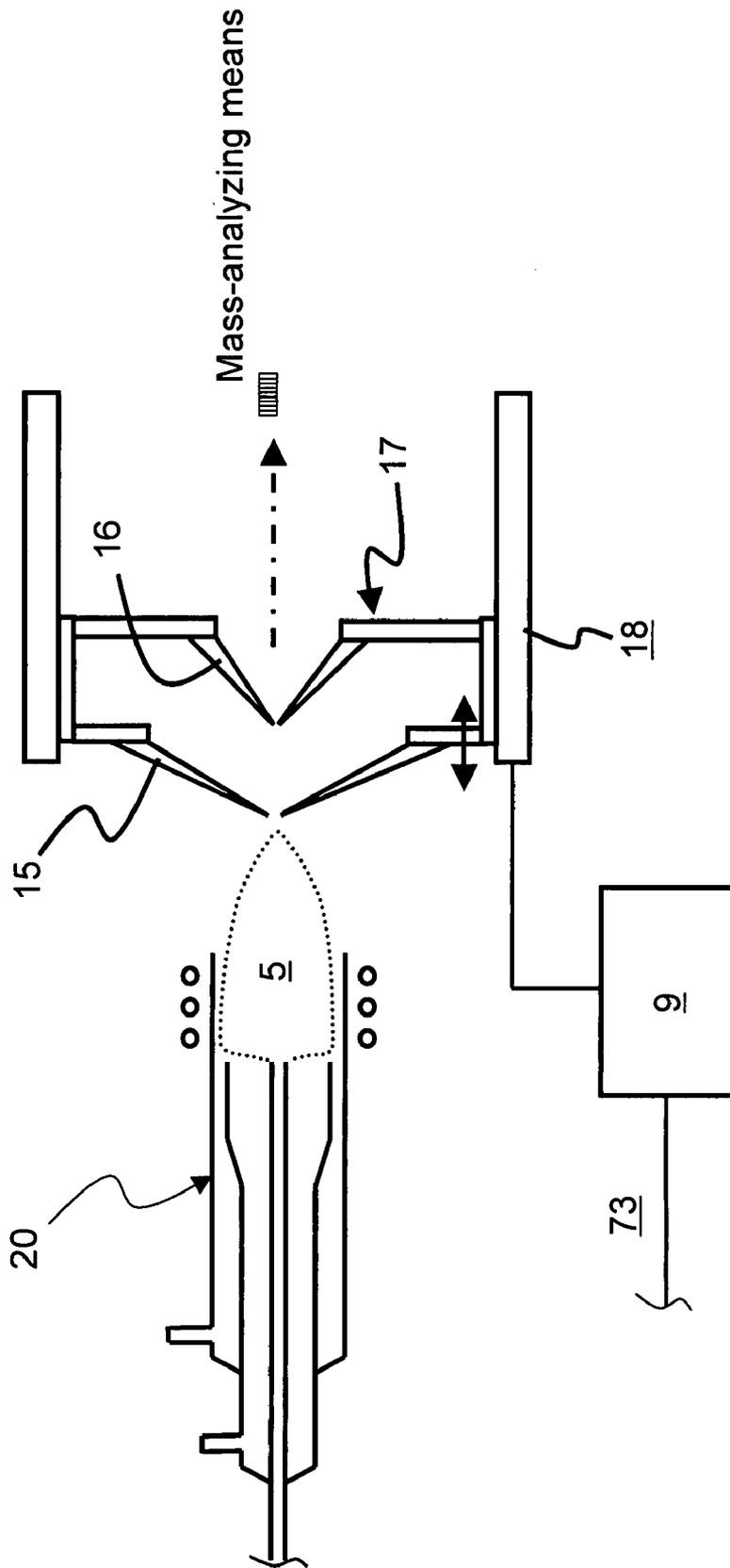
16

17

18

15

5

20

9

73

Fig. 6

INDUCTIVELY COUPLED PLASMA MASS SPECTROMETER

BACKGROUND

1. Field of the Disclosure

The present disclosure relates to technology for an inductively coupled plasma mass spectrometer (ICP-MS), which is a mass spectrometer that uses inductively coupled plasma as the ion source, and in particular, relates to technology for analyzing a high-matrix sample.

2. Discussion of the Background Art

The ICP-MS is known as a high-sensitivity analyzer for detecting traces of metal ions. The basic structure comprises a plasma-generating part for generating plasma from a sample such as a liquid, and a mass-analyzing part for extracting ions from the generated plasma and analyzing these ions.

The plasma-generating part, particularly in the case of a liquid sample, comprises a nebulizer for nebulizing a liquid sample of a certain concentration using a gas having a specific flow rate; a spray chamber for isolating some of the nebulized liquid drops in the form of an aerosol together with an appropriate gas; and a plasma torch such that plasma is generated from the plasma gas and the aerosol is introduced into this plasma.

In further detail, the aerosol is generated by at least some carrier gas being introduced into the nebulizer together with the liquid sample. When this portion of carrier gas blows the liquid sample, the liquid sample is nebulized. The nebulized liquid drops circulate inside the spray chamber. The liquid drops that are relatively large in diameter adhere to the inside walls of the spray chamber and are drained, while only the liquid drops that are relatively small in diameter are transferred toward the plasma torch. In essence, the liquid drops of small diameter, together with the carrier gas for nebulization, form the aerosol and are guided to the plasma torch. The carrier gas is usually an inert gas, typically argon gas.

The plasma torch comprises an inside pipe into which the sample that contains aerosol is introduced and one or multiple outside pipes disposed such that they surround the inside pipe. Auxiliary gas, plasma gas for generating plasma, and the like can be introduced into the outside pipes. Once plasma has been generated by the plasma gas through the operation of a work coil, the aerosol comprising the sample is introduced and as a result, the metal in the sample is ionized and blew out into the plasma.

An interface that faces the generated plasma is disposed at the front end of the mass-analyzing part, which is positioned at the last step of the plasma-generating part. The interface has a two-step structure of a sampling cone and a skimmer cone, and each of these has an orifice for extracting the ions from the generated plasma. Extractor electrodes for extracting the ions in the form of ion beam are disposed at the last step of the interface. The extracted ion beam is introduced into the mass analyzer disposed at the last step and the element is identified due to mass/charge ratio. The analysis results can thereby be obtained in the form of a mass spectrum.

Although well-known throughout industry, an example of the overall structure of an ICP-MS is described in the following JP Unexamined Patent Publication (Kokai) 2000-67804, and the structure of the plasma-generating part is described in JP Unexamined Patent Publication (Kokai) 10-188877. Moreover, JP Unexamined Patent Publication (Kokai) 10-208691 describes technology relating to the use of a plasma-generating part and a mass-analyzing part in combination with one another.

A high-matrix sample is an example of a potential sample to be analyzed by such a device. A "high-matrix sample" is a sample that contains the element to be measured as well as water-soluble substances, such as high concentrations of metal salts. Seawater is an example of a high-matrix sample. When a high-matrix sample is analyzed by conventional methods using conventional devices, there are problems in that, as a result of large amounts of ions being guided to the last step of the device, metal salts and the like are deposited and pollute the surfaces of the sampling cone, skimmer cone, etc., and the orifices become clogged, making analysis impossible. It generally is difficult to analyze a sample in normal mode if the matrix concentration or total dissolved solid (TDS) concentration exceeds 1,000 to 2,000 ppm.

On the other hand, by means of an inductively coupled plasma optical emission spectrometer (ICP-OES), it is possible to analyze even a high-matrix sample having a concentration on the percent order or higher without using a diluting means, which is described later. However, ICP-OES have a disadvantage in that their sensitivity or detection limit is inferior, by three decimal places or more, to inductively coupled plasma mass spectrometers, and it is very difficult to satisfy user requirements for quantitative analysis.

JP Unexamined Patent Publication (Kokai) 8-152408 describes a device comprising an optical measuring device and a mass analyzer for analyzing diverse samples having different matrix concentrations. Nevertheless, the structure of the device described in JP Unexamined Patent Publication (Kokai) 8-152408 is impractical because it is complex and not easy to hold or manipulate, and it does not solve the problem of quantitative analysis.

A single ICP-MS capable of high-sensitivity analysis of liquid samples having a wide range of matrix concentrations would be very effective for practical use. The method whereby a highly concentrated sample that cannot be analyzed directly is diluted to an acceptable extent before aerosol generation is one example. Dilution can be carried out manually or automatically using an autodiluter. JP Unexamined Patent Publication (Kokai) 11-6788 gives an example of a method for diluting a liquid sample using an autodiluter.

Nevertheless, performing dilution by hand takes time. Diluting many samples is an inconvenience in terms of time, and there is also the chance that there will be errors in dilution. On the other hand, using an autodiluter complicates dilution by adding a step for operating additional equipment, and there is the chance that the sample will be contaminated by the outside environment or the tools that are used during dilution of the liquid sample.

An object of the present disclosure is to provide an inductively coupled plasma mass spectrometer with which a user can analyze, continuously and with good reproducibility, samples of various concentrations, including high-matrix samples, without implementing a manual procedure.

SUMMARY OF THE DISCLOSURE

The present disclosure provides an inductively coupled plasma mass spectrometer designed such that an aerosol comprising a carrier gas and liquid drops that contain an analysis sample is introduced into a plasma torch disposed near a work coil connected to a high-frequency power source, a plasma is generated such that it contains the ions of the elements contained in the aerosol, the plasma is projected toward interface having orifices, and at least some of the ions pass and escape through the orifices, this inductively coupled plasma mass spectrometer characterized in that it comprises a control device for comprehensively controlling each of the following

conditions: the amount of liquid drops in the aerosol, the flow rate of carrier gas in the aerosol, the RF output of the high-frequency power source, and the distance between the plasma torch and the interface, wherein the sensitivity to the ions to be measured can be set at a specific level by the control device and the ratio of the maximum and minimum sensitivities to the ions to be analyzed is at least 10:1.

The ratio of the minimum and maximum sensitivities to ions can be further increased and can be brought to at least 20:1.

Moreover, preferably, the user can select any of predetermined multiple combinations of conditions of all factors used for the control. Each of the multiple combinations can be determined as a point, on a sensitivity-oxide ion ratio graph, that corresponds to the analysis conditions relating to at least the flow rate of the carrier gas in the aerosol, the RF output of the high-frequency power source, and the distance between the plasma torch and the interface, with this point falling along a single envelope made up of essentially straight lines wherein the metal oxide ion ratio increases in proportion to sensitivity when the oxide ion ratio is at a minimum for each sensitivity. In this case, each point can also be a point within a specific region on the sensitivity-oxide ion ratio graph.

Furthermore, the carrier gas can comprise a first gas used for the generation of the aerosol and a second gas that is mixed with the resulting aerosol, and the control device can determine the amount of liquid drops to be supplied per unit of time by controlling the flow rates of both the first and second gases. In this case, the control device can operate in such a way that the amount of liquid drops to be supplied per unit of time is changed by changing only the ratio of the flow rates of the first and second gases while keeping constant the total flow rate of these gases.

The distance between the plasma torch and interface can be changed by moving either the plasma torch or the interface in the axial direction.

By means of the inductively coupled plasma mass analyzer of the present disclosure, comprehensively appropriate conditions or parameters are determined for all of the above-mentioned conditions, and the amount of ions that pass through the orifices are adjusted by collective control based on these conditions or parameters; therefore, it is possible for a user to continuously analyze samples of various matrix concentrations, including high-matrix samples, without using additional equipment, such as a liquid dilution means, or without the process taking a long time.

In essence, the inductively coupled plasma mass spectrometer of the present disclosure is capable of easily adjusting the amount of ions that will pass through the interface in accordance with samples of various concentrations, ranging from low-matrix concentration to high-matrix concentration; therefore, it is possible to easily analyze a high-matrix sample with good precision, and it is possible to continuously analyze ordinary samples using the same device. By means of the present disclosure, the amount of ions that will pass through the interface is adjusted by a two-step process of dilution, dilution of aerosol flow and dilution in plasma; therefore, even a high-matrix sample with a sufficiently high concentration (for instance, 20,000 to 30,000 ppm) can be analyzed without using another dilution means.

Moreover, by means of the device of the present disclosure, it is possible to set the control conditions under a relatively high plasma temperature at which oxides and other compounds are not produced in the plasma; therefore, it is possible to eliminate the sensitivity-reducing effect caused by matrix, etc. and to analyze even high-matrix compounds with sufficient sensitivity.

Furthermore, by means of the device of the present disclosure, it is possible to add gas after the aerosol has been generated and control the quantity of flow in combination with the gas used during aerosol generation; therefore, it is possible to set control conditions, including the effect of the carrier gas in the aerosol on the plasma, and in particular, to change the liquid drop content of the aerosol without changing the carrier gas total flow rate.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a drawing showing the structure surrounding the plasma-generating part of the inductively coupled plasma mass spectrometer of the present disclosure.

FIG. 2 is a graph showing the so-called sensitivity-oxide ion ratio property.

FIG. 3 is a drawing describing how parameters that affect a sample in a plasma state are set; table (a) gives the condition settings of multiple modes that can be selected in accordance with samples of different matrix concentrations, and (b) shows the position on the graph of the sensitivity-oxide ion ratio corresponding to each mode.

FIG. 4 presents a table and a drawing similar to FIG. 3 showing the parameter settings when the output of the high-frequency power source is fixed.

FIG. 5 presents a table showing an example of how parameters that affect a sample in an aerosol state are set; tables (a) and (c) give examples of settings when the carrier gas total flow is fixed at a predetermined value, and table (b) gives an example of settings that includes a step for changing the carrier gas total flow.

FIG. 6 is a drawing describing other means for changing the sampling depth Z.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The inductively coupled plasma mass spectrometer of a preferred embodiment of the present disclosure will now be described in further detail while referring to the attached drawings. FIG. 1 is a drawing showing primarily the plasma-generating part of the body of the inductively coupled plasma mass spectrometer of the present disclosure. It also shows the structure of the control system in combination with each element. It should be noted that the term "dilution" in the description of the mode of operation of the present disclosure includes all means by which the amount of sample ions that pass through the interface part can be reduced, and in places other than the description of the prior art, also refers to so-called "dry" dilution by which a liquid is not used.

As previously described, this type of inductively coupled plasma mass spectrometer comprises a mass-analyzing part at the last step of the plasma generating part. FIG. 1 shows only a sampling cone 15 and a skimmer cone 16 of the mass-analyzing part, and these parts are at the front thereof and form the interface part that acts to isolate the ion beam. Although not illustrated, the ion beam that is led toward the back of skimmer cone 16 are guided to the mass spectrometer that is positioned farther back. The ion beam is thereby separated based on their mass-charge ratio, and the element is identified.

The primary structural elements of a plasma-generating part 10 are an aerosol-generating means 30 and a plasma torch 20. Aerosol-generating means 30 comprises a nebulizer 40 for nebulizing a liquid sample and a spray chamber 50 for circulating the nebulized liquid sample and isolating only the liquid drops that are relatively small in diameter.

A liquid sample **61** and a gas **76A** for generating the aerosol are fed to nebulizer **40**. Liquid sample **61** can be nebulized by blowing gas **76A** at a specific flow rate onto liquid sample **61**. An inert gas, typically argon gas, is used to generate the aerosol. Control of the amount of gas supplied is discussed later.

Liquid sample **61** is fed by liquid sample control means **60**. Liquid sample control means **60** comprises a vessel **62** in which the liquid sample is stored and a peristaltic pump **63** disposed at a position along the piping. Peristaltic pump **63** is controlled by a control part **64**. In essence, control part **64** controls peristaltic pump **63** in such a way that the pump supplies the necessary amount of liquid sample **61** from vessel **62** to nebulizer **40**.

Spray chamber **50** houses a chamber **51** through which the nebulized liquid drops are capable of circulating. A cylindrical wall **52** is formed inside chamber **51** such that gas flows in the opposite directions inside and outside the wall **52**. The nebulized liquid drops are transported by the gas flow. However, the liquid drops that are relatively large in diameter adhere to the inner wall surface of chamber **51** and are discharged through a drain **53**. The liquid drops of a relatively small diameter are emitted as aerosol through a connecting opening **54** in the direction of a connecting pipe **31**.

Aerosol is fed through connecting pipe **31** to plasma torch **20**. It should be noted that an inlet **32** for an additional diluting gas **76B** that is added for dilution is disposed in the middle of connecting pipe **31**. The effect of additional diluting gas **76B** is discussed later.

Plasma torch **20** comprises first and second outside pipes **22** and **23** on the outside of an inside pipe to which aerosol is introduced. An auxiliary gas (or a middle gas) **77A** is introduced into first outside pipe **22**, and a plasma gas **77B** is introduced into outermost second outside pipe **23**. A work coil **25** is disposed at the tip of plasma torch **20**. Work coil **25** is connected to a high-frequency power source (RF power source) **80** via a matching box **81**.

Work coil **25** provides plasma torch **20** with the energy for generating a plasma **5**. It is possible to bring plasma **5** to an ignited state by turning on high-frequency power source **80** after auxiliary gas **77A** and plasma gas **77B** have been supplied to plasma torch **20**. Then the aerosol containing the liquid drops of liquid sample is supplied from inside pipe **21** in order to analyze the sample. As a result, the elements present in the liquid drops of the aerosol are ionized in plasma **5**.

It is possible to increase or decrease the number of ions that pass through interface **15** and **16** by changing the output of high-frequency power source **80**. It is possible to reduce the number of ions that pass through interface **15** and **16** by raising the output of high-frequency power source **80** under the specific conditions described later in relation to the oxide ion-ratio graph.

By means of the present embodiment, plasma torch **20** is anchored on a table **26**, which can be moved by a drive mechanism **27**, such as a motor. As a result, plasma torch **20** can be moved along the direction of introducing aerosol. This adjusts the distance Z between plasma torch **20** and interface **15** and **16** (sampling depth). An X-Y stage is typically used as table **26**. Drive mechanism **27** is controlled by a control part **90**. FIG. **1** shows only plasma torch **20** anchored to table **26**, but it is possible to anchor to the table, in addition to plasma torch **20**, other parts of the system that include spray chamber **50** and nebulizer **40**, such that these parts can be moved by drive mechanism **27**, too.

In general, the amount of ions that pass through interface **15** and **16** shows a tendency toward increasing as the distance

Z between the two becomes shorter, and the amount of ions that pass through shows a tendency toward decreasing as distance Z becomes longer. Consequently, it is possible to adjust the number of ions that pass through interface **15** and **16** by adjusting distance Z between the plasma torch **20** and the interface.

One characterizing feature of the present disclosure is that it is possible to easily and with good reproducibility dilute the liquid sample, such as a high-matrix sample, by appropriately controlling both the carrier gas that forms the aerosol and the plasma comprising ions of the metal that is contained in the aerosol. In essence, by means of the control system of the present disclosure, a time-consuming diluting process using a liquid is unnecessary and the procedure that must be conducted by a user is very simple. The effect of the control system of the present embodiment will now be described.

The inductively coupled plasma mass spectrometer of the present embodiment comprises a control device **70**, a memory **95** connected to the control device, and a user interface **100**. Control device **70** is designed such that control signals **73A**, **73B**, and **73C** are sent to control part **90** for controlling high-frequency power source **80** and drive mechanism **27**, and control part **64** for controlling peristaltic pump **63** for supplying liquid sample **61**. Furthermore, control device **70** also comprises a gas control part **79** for controlling gas.

Gas control part **79** can send control signals **71A**, **71B**, **72A** and **72B** to gas flow rate control devices **74A**, **74B**, **75A**, and **75B**. Control signals **71A** and **71B** determine the amount of aerosol-generating gas **76A** and additional diluting gas **76B** to be fed to the respective gas flow rate control devices **74A** and **74B**, and control signals **72A** and **72B** determine the amount of auxiliary gas **77A** and plasma gas **77B** to be fed to gas flow rate control devices **75A** and **75B**.

Control device **70** can comprise one or multiple ICs. Moreover, control device **70** can be designed as a computer having a display that is obtained by combining, as one unit with or separate from, user interface **100**. Memory **95** can be designed as a memory that can be written over. It is shown memory **95** is connected to the control device in FIG. **1**, but it can also be designed such that it is connected with user interface **100**.

The memory **95** is an example of a computer readable medium. A computer readable medium can be a single medium or multiple media as is understood by those in the art. The computer readable medium can be designed as the type that can be written over and can be connected to or combined with the control device **70** for providing instructions to the control device **70**.

Gas control part **79** can control the spectrometer in such a way that dilution is performed in an aerosol state. As shown in the drawing, it is possible to add additional diluting gas **76B** to the aerosol transferred from spray chamber **50** and reduce the ratio of liquid drops of liquid sample to the total amount of carrier gas. When dilution in the aerosol step is not necessary, such as in the case of analysis of a low-matrix sample, only aerosol-generating gas **76A** serves as the carrier gas for the aerosol. On the other hand, in the case of analysis of a high-matrix sample, it is possible to dilute the aerosol by adding additional diluting gas **76B**. In the latter case, both the aerosol-generating gas and the additional diluting gas serve as the carrier gas.

In essence, by means of the present disclosure, the ratio of liquid drops contained in the aerosol that reaches plasma torch **20** and the flow rate of the carrier gas can be determined comprehensively but on a one-to-one basis by controlling the amount of liquid sample **61** to be fed via control signal **73C**

and by controlling the flow rate of aerosol-generating gas **76**A and additional diluting gas **76**B via control signals **71**A and **71**B.

Therefore, when recording the relationship of the liquid drop content ratio in the aerosol with the flow rate of aerosol-generating gas **76**A and/or the amount of liquid sample fed, it is possible to numerically convert the degree to which the aerosol is diluted by adding the flow rate of the diluting additional gas **76**B to the flow rate of the carrier gas. This numerical conversion is an effective means for guaranteeing a good reproducibility of dilution.

Performing controllable dilution after aerosol generation is also effective in terms of controlling the plasma **5**, which is discussed later. When there is no means for feeding additional diluting gas **76**B, the liquid drop content is changed by reducing the amount of aerosol-generating gas fed during aerosol generation, which should reduce the amount of the sample, and the total flow as carrier gas is also reduced by approximately the same ratio as the sample amount is reduced. As a result, the extent to which plasma **5** generated by plasma torch **20** is cooled by the carrier gas of the aerosol is reduced. In this case, it eventually becomes very difficult to control with good precision the amount of ions that pass through interface **15** and **16**.

Even if the amount of aerosol-generating gas that is supplied has been reduced, the device of the present disclosure makes it possible to add the appropriate amount of additional diluting gas. Therefore, it is possible to feed to plasma torch **20** an aerosol that is different only in terms of the liquid drop content without changing the flow rate of carrier gas in the aerosol and thereby guarantee sufficient reproducibility of the analysis results.

The fundamental data for controlling each gas by gas control part **79** can be directly input using user interface **100**, or it can be pre-stored in memory **95**. Although not illustrated, user interface **100** can comprise an input device and a display for displaying input and control status, and similar operations.

FIG. **2** is a graph showing the so-called sensitivity-oxide ion ratio property that is referred to in order to determine the control factors of the present disclosure. This graph of the sensitivity-oxide ion ratio shows the detection sensitivity for a specific ion on the x axis, and the oxide ion ratio of the ion in question represented on the y-axis as a logarithm. The region enclosed by the curved lines in the figure shows the distribution of measurement points when the above-mentioned factors, in essence, the carrier gas flow rate, the high-frequency power source output, and the distance Z between the plasma torch and interface, are changed as variable parameters. By means of the present embodiment, Ce (cerium) is used as the specific ion, but it is also possible to use Ba (barium) or La (lanthanum). Moreover, the indicator is not limited to the oxide ion ratio and can be a ratio of sensitivity for ions and another compound that is an indicator of a physical phenomenon as represented by the present disclosure.

By means of the present disclosure, control is possible by providing that the control parameters can be constantly regulated. This regulation capacity is derived from the sensitivity-oxide ion ratio. As illustrated, the measurement points are distributed within region R**1** sandwiched between the two curved lines. By means of the present disclosure, each of the above-mentioned parameters is set such that they become points along arrow S when positioned at the bottom of an outside envelope **110**. In other words, by means of the present disclosure, all of the factors controlled by the control device are set such that, on the sensitivity-oxide ion ratio curve showing the relationship between the sensitivity for a specific

metal ion and oxide ions of the metal ion, they conform to conditions that are found along the envelope wherein the log of the oxide ion ratio is virtually proportional to sensitivity when the oxide ion ratio is at virtually the minimum for each sensitivity.

In essence, by means of the device of the present disclosure, it is possible to change only the amount of liquid drops without changing the total flow rate of carrier gas in the aerosol that is supplied, and it is possible to change the carrier gas flow rate without changing the amount of liquid drops supplied per unit of time. In the latter case, the plasma temperature and plasma status change in accordance with the flow rate of the carrier gas.

Nevertheless, when the plasma temperature is particularly low, the matrix element bonds with other elements so that it is not in pure element ion state and interference is produced that becomes an impediment to analysis of the element to be measured. This state is undesirable when unintentionally produced, particularly when the object is analysis of a specific element. Therefore, whether the total flow rate of carrier gas is low or high, the above-mentioned parameters are set such that temperature of the plasma (particularly the gas temperature) does not fall. For example, in the case of the present embodiment it is possible to determine a point corresponding to a combination of control parameters as a point on the inside of region R**2**, which is demarcated by a predetermined oxide ion ratio and sensitivity as shown by the parallelogram in the graph in FIG. **2**. The region can be determined by a variety of methods, such as satisfying a specific numerical relationship, or setting a specific numerical range.

By using this parameter setting method, it is possible to maintain a relatively high gas temperature during analysis, and to prevent negative effects on analysis precision as a result of the element to be measured forming other compounds, whether the flow rate of the carrier gas is relatively low, or vice-versa, the flow rate of carrier gas has been increased for dilution, as will be discussed later.

As previously mentioned, when the variable parameters are determined by direct input by a user, it is possible to reject the use of the input value if the input value is outside a predetermined range (for instance, outside region R**2** in FIG. **2**). In essence, for instance, if user interface **100** determines that an input parameter is inappropriate after parameters have been input in succession, it is possible to reject the parameter, or another possible example is the use of an alarm once all of the parameters have been input. On the other hand, when the device of the present disclosure is designed such that each variable parameter is pre-stored in memory **95**, it is possible to select a group of stored parameters that satisfies the above-mentioned conditions. An example of how parameters are set is described below.

FIG. **3** shows the parameters of each condition that affects the sample when in a plasma state, and provides a drawing showing an example of condition settings when these parameters change. Table (a) shows the condition settings of the multiples modes that can be selected in accordance with samples having different matrix concentrations, and (b) shows the position on the graph of the sensitivity-ion oxide ratio corresponding to each mode.

The numbers corresponding to each mode shown in FIG. **3**(*a*) can be stored in a readable memory together with each parameter that will affect the aerosol that is discussed later. By means of the present example, the number of modes is 5, although the number can be decreased or vice-versa, the number of modes can be increased. It is even possible to change parameters virtually continuously within a specific range. It should be noted that by means of the present

example, carrier gas is fed with the total amount of carrier gas serving as the aerosol-generating gas, and the amount of liquid sample supplied by the peristaltic pump is also constant.

In the table shown in FIG. **3**, mode **1** is on the high-sensitivity side and mode **5** is on the low-sensitivity side. In essence, a low-matrix sample is analyzed using the modes beginning from mode **1**, while a high-matrix sample is analyzed using the modes beginning from mode **5**. When attention is focused on the sensitivity for cerium ions in the table, it is clear that a sensitivity ratio exceeding 4:1 is manifested between mode **1** and mode **5**.

On the other hand, according to FIG. **3**(*b*), the points corresponding to each mode are points along the envelope at the bottom of the sensitivity-oxide ion ratio graph. Consequently, as previously mentioned, the detrimental effects of oxides, and the like on the analysis results can be minimized in each mode.

FIG. **4** shows another example of how parameters are set. Table (a) shows the condition settings of the multiple modes that can be selected in accordance with samples having different matrix concentrations, and (b) shows the position on the graph of the sensitivity-ion oxide ratio corresponding to each mode. By means of the present example, the output of the high-frequency power source (RF output) is constant, as shown in (a), and a difference in sensitivity is realized by changing the other parameters.

As in FIG. **3**, a low-matrix sample is analyzed using the modes beginning from mode **1** in FIG. **4**, while a high-matrix sample is analyzed using the modes beginning from mode **6**. Comparison of the cerium ion concentration in mode **1**, in which maximum sensitivity is obtained, and that in mode **6**, in which minimum sensitivity is obtained, reveals that the sensitivity ratio exceeds 4:1 (is at least 6:1 or greater). Moreover, as in FIG. **3**, the points corresponding to each mode on the sensitivity-oxide ion ratio graph are points along the envelope at the bottom, as shown in FIG. **4**(*b*).

In contrast to the fact that FIGS. **3** and **4** present tables showing the condition settings of parameters that affect a sample in a plasma state, FIG. **5** presents tables showing an example of condition settings of parameters that affect a sample in an aerosol state. For instance, when the sample to be analyzed is a low-matrix sample, it is not known whether it is necessary to dilute the aerosol emitted from the spray chamber, but when the sample to be analyzed is a high-matrix sample, diluting gas is added to the aerosol, and there may even be cases in which further dilution is required. Each table in FIG. **5** shows the extent of aerosol dilution in accordance with the amount of diluting gas added.

Three types of settings are shown in FIG. **5**. Table (a) is an example of settings wherein the carrier gas total flow rate was fixed at 1.05 mL/minute, table (b) is an example of settings including a step wherein the carrier gas total flow rate was changed from 1.05 mL/minute to 0.95 mL/minute, and table (c) is an example of settings wherein the carrier gas total flow rate was fixed at 0.95 mL/minute. These settings are examples and a variety of other settings are possible.

The important point is that once the carrier gas flow rate has been set by the method illustrated in FIGS. **3** and **4**, the carrier gas flow rate is affected such that the aerosol dilution is multiplied. In essence, when determining the extent of dilution, first the appropriate extent of dilution is determined for parameters that affect the plasma shown in FIGS. **3** and **4** and then the parameters that affect the aerosol are determined from the table shown in FIG. **5** by multiplying by the first extent of dilution.

A specific example is the interaction between parameters that affect the plasma shown in FIGS. **3** and **4** and parameters that affect the aerosol shown in FIG. **5**. For instance, in mode **4** shown in FIG. **3**(*a*), the total flow rate of carrier gas is 1.05 mL/minute, and of the series of mode settings, sensitivity is approximately half that of mode **1**, which has the maximum sensitivity. This means that the amount of sample ions that pass through the interface is reduced by approximately half by changing only the parameters that affect plasma.

In this case, further dilution is possible by appropriately selecting the parameters shown in FIG. **5**. As previously described, the carrier gas total flow rate is 1.05 mL/minute in each of the series of modes shown in FIG. **5**(*a*). Therefore, dilution can be performed whereby in mode **4** in FIG. **3**(*a*), the system is initially set at mode A in FIG. **5**(*a*), and then sensitivity is changed by ½, in essence, the amount of sample ions that pass through the interface is changed by ½, by staying in mode **4** but changing the mode in FIG. **5**(*a*) to mode B, and as a result, it is possible to dilute the sample to ¼ the maximum dilution.

In another case it is possible to change both of these modes. For instance, by changing from mode **4** to mode **5** in FIG. **3**(*a*), it is possible to change dilution from approximately 12 that of mode **1** to approximately ¼. In this case, the carrier gas total flow rate changes from 1.05 mL/minute to 0.95 mL/minute. Therefore, in Table 5, a mode change corresponding to such a mode change is selected from the tables in FIG. **5**.

For instance, using the series of modes in FIG. **5**(*b*), once the initial setting has been brought to mode A where the carrier gas total flow rate is 1.05 mL/minute, it changes to mode B where the total carrier gas flow rate is 0.95 mL/minute to meet the change from mode **4** to mode **5**. As a result, a dilution of approximately ⅛ can be accomplished by multiplying a dilution of approximately ¼ through selection of mode **5** by a dilution of approximately ½ by selection of mode B.

As previously described, a variety of dilutions are possible by changing the parameters that affect the plasma in conjunction with the parameters that affect the aerosol. Both have different physical effects on the sample and therefore, the appropriate parameter settings can be selected in accordance with the sample to be analyzed. The parameters in the tables shown in FIGS. **3** through **5** are for illustration, and a variety of different dilution conditions can be provided by storing many parameters in the memory and reading these parameters as necessary.

When use is limited and more than certain necessary types of combinations of parameters are not needed, it is possible to predetermine several types of combinations of parameters that will affect the plasma and parameters that will affect the aerosol, store only these in memory **95**, and read these combinations.

FIG. **6** is a drawing describing an embodiment that is a modified version of FIG. **1**, and shows other means for changing the sampling depth Z. As previously described, in the embodiment in FIG. **1**, interface **15** and **16** are stationary, and plasma torch **20** can move relative to interface **15** and **16**. In the embodiment in FIG. **6**, on the other hand, plasma torch **20** is stationary, and interface **15** and **16** can move with respect to plasma torch **20**.

As shown in FIG. **6**, sampling cone **15** and skimmer cone **16** are a single unit, and this unit **17** is guided by a guide means that is not illustrated such that it can move within a frame **18**. For instance, a drive mechanism that is not illustrated is disposed on the side of frame **18** and this drive mechanism is controlled by a control part **91**. It should be

noted that the pressure is reduced between sampling cone **15** and skimmer cone **16**, and pressure is further reduced to a high vacuum in the last step of skimmer cone **16**. However, these means are not shown in FIG. **6**.

The above-described examples are preferred working examples of the present disclosure, but it goes without saying that they are only examples and in no way limit the present disclosure. Various modifications and changes by persons skilled in the art are possible.

What is claimed is:

1. An inductively coupled plasma mass spectrometer designed such that an aerosol comprising a carrier gas and liquid drops containing an analysis sample is introduced into a plasma torch disposed near a work coil connected to a high-frequency power source, a plasma is generated such that it contains the ions of the elements contained in the aerosol, the plasma is projected toward interface having orifices, and at least some of the ions pass and escape through the orifices, said inductively coupled plasma mass spectrometer comprising:

a control device for comprehensively controlling conditions of the inductively coupled plasma mass spectrometer according to instructions in a computer readable medium;

the computer readable medium containing the instructions for instructing the control device to comprehensively control each of the following conditions: the amount of liquid drops in the aerosol, the flow rate of carrier gas in the aerosol, the RF output of the high-frequency power source, and the distance between the plasma torch and the interface, wherein the sensitivity to the ions to be measured can be set at a specific level by the control device and the ratio of the maximum and minimum sensitivities to the ions to be analyzed is at least 10:1; and wherein

the computer readable medium further contains instructions for instructing the control device to determine at least the flow rate of carrier gas in the aerosol, the RF output of the high-frequency power source, and the distance between the plasma torch and the interface such that the points corresponding to the analysis conditions on a sensitivity/oxide ion ratio graph showing the relationship between sensitivity to a specific metal ion and oxide ions of the metal ion are positioned along an envelope wherein the log of the ratio of oxide ions forms a virtually proportional relationship with sensitivity

when the oxide ion concentration at each sensitivity has been brought to virtually a minimum.

2. The inductively coupled plasma mass spectrometer according to claim **1**, wherein the computer readable medium further contains instructions for instructing the control device to determine at least the conditions of the flow rate of carrier gas in the aerosol, the RF output of the high-frequency power source, and the distance between the plasma torch and interface such that the points corresponding to the analysis conditions are positioned within a specific region on the sensitivity/oxide ion ratio graph.

3. The inductively coupled plasma mass spectrometer according to claim **1**, wherein said carrier gas comprises a first gas used for generation of the aerosol and a second gas that is added and mixed after the aerosol has been generated, and the computer readable medium further contains instructions to control the control device to control the liquid drop content of the aerosol by controlling the flow rates of the first and second gases.

4. The inductively coupled plasma mass spectrometer according to claim **3**, wherein said ratio of the maximum and minimum sensitivity at each position along the envelope is at least 4:1 at condition settings under which there is no change in the amount of second gas.

5. The inductively coupled plasma mass spectrometer according to claim **4**, wherein the computer readable medium further contains instructions to control said control device such that the amount of liquid drops to be supplied per unit of time to the plasma torch is changed by changing the ratio of the flow rates of the first and second gases while keeping constant the total flow rate of these gases.

6. The inductively coupled plasma mass spectrometer according to claim **5**, wherein the computer readable medium further contains instructions to control said control device to bring the ratio of the maximum and minimum amounts of liquid drops to be supplied per unit of time to the plasma torch to at least 5:1 by changing only the ratio of the flow rates of the first and second gases while keeping constant the total flow of these gases.

7. The inductively coupled plasma mass spectrometer according to claim **1**, wherein the computer readable medium further contains instructions to change the distance between the plasma torch and the interface by moving either the plasma torch or the interface in the axial direction.

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